Bimetallic-Catalyzed Reduction of Carboxylic Acids and Lactones to Alcohols and Diols

Arno Behr,* Volker A. Brehme

Lehrstuhl für Technische Chemie A, Universität Dortmund, Emil-Figge-Str.66, 44227 Dortmund, Germany
Fax: (+49) 231-755-2311, e-mail: behr@ct.uni-dortmund.de

Received: December 24, 2001; Accepted: March 7, 2002

Abstract: The homogeneously catalyzed reduction of carboxylic acids with hydrogen was studied. Bimetallic catalysts consisting of a group 8 or 9 late transition-metal and a second group 6 or 7 transition-metal carbonyl showed a synergistic effect allowing the conversion in good yields under moderate conditions. Besides the effect of different catalyst precursors, the influence of temperature, hydrogen pressure, and catalyst concentration was investigated. An equimolar mixture of $[Rh(acac)(CO)_2]$ and $[Mo(CO)_6]$ showed the highest activity and was therefore applied to the reduction of lactones to diols. The reduction potential of the catalyst was found to be dependent on the ring size of the lactone used. Five-membered ring lactones were hardly converted to diols whereas six- and seven- membered ring lactones reacted easily.

Keywords: bimetallic catalysts; carboxylic acids; homogeneous catalysis; hydrogenation; lactones

Introduction

Hydrogenation of fatty acids and their derivatives to fatty alcohols is an industrially important process. Usually this reaction is carried out with heterogeneous copper-containing, mixed-oxide catalysts at 200 – 300 °C and 20 – 30 MPa requiring expensive high-pressure reactors.[1] Several approaches have been made using homogeneous reduction catalysts which allow more moderate reaction temperatures and hydrogen pressures. Piacenti et al.[2] reported the use of cluster ruthenium carbonyl hydrides to reduce saturated monocarboxylic acids up to C_6 to the corresponding alcohols at 100 – 200 atm of hydrogen and 100 – 200 °C. Phosphine-modified ruthenium catalysts were used by Elsevier et al.[3] in the reduction of esters to alcohols. Dimethyl oxalate is reduced to ethylene glycol at 100 °C and 70 bar hydrogen pressure with TOF's {turn over frequency: n(product)/[n(catalyst) × time]} up to 54 h^{-1}. For the case of the reduction of benzyl benzoate to benzyl alcohol an increase in activity is observed by using a fluorinated alcohol as solvent and triethylamine as additive. TON's [turn over number: n(product)/n(catalyst)] of 2000 are possible.

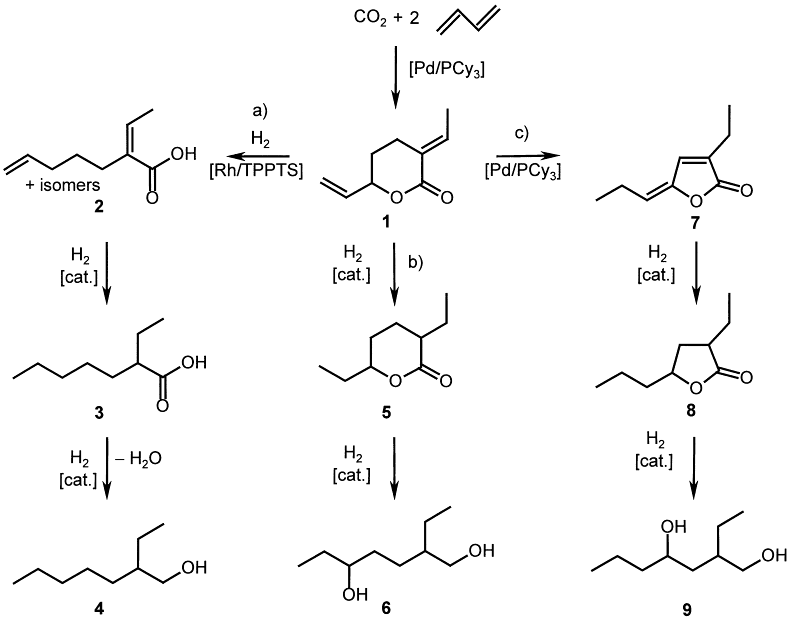
Another possibility is the application of bimetallic catalysts. There are several examples in the literature reporting a synergistic effect by the reduction of a carboxylic group to the corresponding alcohol. The reduction of decanoic acid with a rhenium/osmium bimetallic catalyst was described by Yoshino et al.[4] At hydrogen pressures from 25 – 100 atm and temperatures from 100 – 120 °C decanol is formed in selectivities up to 85%. Some esters and hydrocarbons were detected as by-products. In a patent application,[5] a synergistic effect of a heterogeneous catalyst comprised of a first component which is either molybdenum or tungsten and a second component of group 8 of the periodic table is reported. The reduction of carboxylic acids from C_2 to C_{12} at 200 – 300 °C and elevated hydrogen pressure leads to the corresponding alcohols and esters.

Fuchikami et al.[6] introduced a bimetallic system consisting of a group 8 – 10 late transition metal and a group 6 or 7 transition metal carbonyl. The group 8 – 10 metals are used as homogeneously soluble compounds or heterogeneously dispersed on various supports like alumina or charcoal. Pentadecanoic acid is reduced at 140 – 180 °C and 100 atm hydrogen pressure giving up to 99% pentadecanol. In addition, dicarboxylic acid monomethyl esters are reduced to ω-hydroxycarboxylic esters with yields in the range of 81 – 91%.

It is well known that catalysts that are able to reduce carboxylic acids to alcohols are also active in the reduction of lactones to diols. We applied the reduction catalysts to the reduction of 2-ethylheptanol (**3**), 2-ethylheptan-5-olide (**5**) and 2-ethylheptan-4-olide (**8**). All these compounds are produced by a simple synthesis starting with a homogeneously catalyzed telomerization of 1,3-butadiene with carbon dioxide giving the δ-lactone (**1**) (Scheme 1).

Biphasic hydrogenation with a rhodium/TPPTS catalyst gives an isomeric mixture of the unsaturated carboxylic acids **2**.[7] Heterogeneous hydrogenation leads to 2-ethylheptanoic acid. Heterogeneous hydrogenation of δ-lactone **1** gives a diastereomeric mixture

1615-4150/02/34405-525 – 532 $ 17.50+.50/0



Scheme 1. Telomerization of butadiene with carbon dioxide and hydrogenation giving different products.

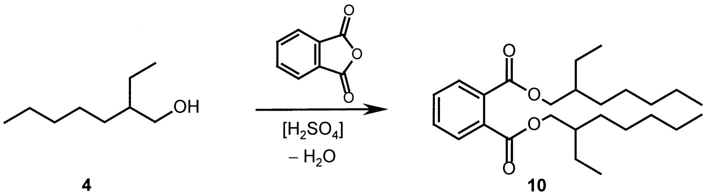
of 2-ethylheptane-5-olide (**5**).[8] The γ-lactone **7** is produced by isomerization of **1** with a palladium/tricyclohexylphosphine catalyst,[9] hydrogenation with standard heterogeneous catalysts gives **8** in high yields.

Our intention is to provide a convenient reaction pathway for the production of 2-ethylheptanol (**4**), 2-ethyl-1,5-heptanediol (**6**), and 2-ethyl-1,4-heptanediol (**9**) by simple reduction with hydrogen of the corresponding precursors.

2-Ethylheptanol (**4**) is an interesting softener alcohol for the production of di(2-ethylheptyl) phthalate (**10**) which could be used as plasticizer[10] for PVC (Scheme 2).

Since the commercially available product di(2-ethylhexyl) phthalate (DEHP) was found to be one of the more toxic phthalates,[11] the interest in alternative compounds has increased. Compared to DEHP, di(isononyl) phthalate (DINP) poses no risk to human reproduction or development. Presumably di(2-ethylheptyl) phthalate is in the same way harmless due to the same number of carbon atoms.

The products 2-ethyl-1,5-heptanediol (**6**) and 2-ethyl-1,4-heptanediol (**9**) are interesting starting materials for new polyesters and polyurethanes.[12]



Scheme 2. Synthesis of di(2-ethylheptyl) phthalate softener.

Results and Discussion

Reduction of 2-Ethylheptanoic Acid to 2-Ethylheptanol

At first, the reduction of 2-ethylheptanoic acid to 2-ethylheptanol with single homogeneous or heterogeneous catalysts was investigated. Several rhodium- and ruthenium-based catalysts and molybdenum hexacarbonyl were studied (Table 1).

Neither a single homogeneous catalyst nor a single heterogeneous catalyst achieved yields higher than 10% of 2-ethylheptanol (**4**). Within these catalysts the ruthenium-based precursors are the more active ones.

To increase the yield of 2-ethylheptanol a second catalyst precursor was added. The results of the bimetallic reduction with homogeneously dissolved catalysts are summarized in Table 2.

Catalyst 1 consists of a transition-metal carbonyl of group 6 or 7. Additionally, the known hydroformylation catalyst [Co_2CO_8] and the non-toxic Mo(II) acetate were used. Catalyst 2 was preferably a homogeneously soluble rhodium compound like [Rh(acac)$(CO)_2$] or metals which were heterogeneously dispersed on alumina or charcoal. Ruthenium compounds were applied because of their ability to reduce carboxylic acids to alcohols without further additives.[2]

By applying bimetallic catalysts nearly quantitative yields are possible. Comparing the catalytic activities of different carbonyl complexes in the bimetallic reduction with [Rh(acac)$(CO)_2$] as second catalyst at 200 °C and 150 bar hydrogen pressure leads to the following sequence with decreasing activity:

Table 1. Reduction of 2-ethylheptanoic acid with homogeneous and heterogeneous catalysts.[a]

Run	Catalyst	Temperature [°C]	Pressure H_2 [bar]	Conversion (**3**) [%]	Yield (**4**) [%]
1/1	$[Mo(CO)_6]$	200	150	2	2
1/2	$[Rh(acac)(CO)_2]$	200	150	0	0
1/3	$[Ru(acac)_3]$	200	150	5	5
1/4	Rh/C	200	150	0	0
1/5	Rh/Al_2O_3	200	150	0	0
1/6	Ru/C	200	150	10	10

[a] Conditions: time t = 2 h, stirrer velocity = 600 rpm; m(**3**) = 2 g; n(**3**) = 12.6 mmol, n(catalyst) = 0.126 mmol = 1 mol %; m(dioxane) = 40 g.

Table 2. Reduction of 2-ethylheptanoic acid (3) with homogeneous bimetallic catalysts.

Run	Catalyst 1	Catalyst 2	Temperature [°C]	Pressure H_2 [bar]	Time [h]	Yield (**4**) [%]
2/1	$[Mo(CO)_6]$	$[Rh(acac)(CO)_2]$	150	150	4	37
2/2	$[Mo(CO)_6]$	$[Rh(acac)(CO)_2]$	150	150	20	84
2/3	$[W(CO)_6]$	$[Rh(acac)(CO)_2]$	150	150	4	0
2/4	$[Re_2(CO)_{10}]$	$[Rh(acac)(CO)_2]$	150	150	4	9
2/5	$[Cr(CO)_6]$	$[Rh(acac)(CO)_2]$	200	150	2	3
2/6	$[Mo(CO)_6]$	$[Rh(acac)(CO)_2]$	200	50	2	0
2/7	$[Mo(CO)_6]$	$[Rh(acac)(CO)_2]$	200	75	2	16
2/8	$[Mo(CO)_6]$	$[Rh(acac)(CO)_2]$	200	100	2	39
2/9	$[Mo(CO)_6]$	$[Rh(acac)(CO)_2]$	200	150	2	88
2/10	$[Mo(CO)_6]$	$[Rh(acac)(CO)_2]$	200	150	4	99
2/11	$[Mo(OAc)_2]_2$	$[Rh(acac)(CO)_2]$	200	150	2	5
2/12	$[W(CO)_6]$	$[Rh(acac)(CO)_2]$	200	150	2	4
2/13	$[Mn_2(CO)_{10}]$	$[Rh(acac)(CO)_2]$	200	150	2	6
2/14	$[Re_2(CO)_{10}]$	$[Rh(acac)(CO)_2]$	200	150	2	62
2/15	$[Co_2(CO)_8]$	$[Rh(acac)(CO)_2]$	200	150	2	0
2/16	$[Mo(CO)_6]$	$[Ru(acac)_3]$	200	150	2	28
2/17	$[Mo(CO)_6]$	$[Co_2(CO)_8]$	200	150	2	6
2/18	$[Mo(CO)_6]$	$[RhCl_3 \cdot 3\,H_2O]$ [a]	200	150	2	0
2/19	$[Mo(CO)_6]$	$[Rh(cod)Cl]_2$	200	150	2	0
2/20	$[Mo(CO)_6]$	$[Rh(OAc)_2]_2$	200	150	2	48
2/21	$[Mo(CO)_6]$	$[Rh(acac)_3]$	200	150	2	11
2/22[b]	$[Mo(CO)_6]$	$[Rh(acac)(CO)_2]$	190	150	4	95

acac: acetylacetonate; OAc: acetate; cod: cyclooctadiene. Conditions: stirrer velocity = 600 rpm; m(**3**) = 2 g; n(**3**) = 12.6 mmol; n(catalyst 1) = n(catalyst 2) = 0.126 mmol (= 1 mol %); m(dioxane) = 40 g.

[a] To dissolve $[RhCl_3 \times 3\,H_2O]$ in dioxane 0.27 g water (0.015 mol) were added.

[b] m(**3**) = 15.0 g; n(**3**) = 94,.8 mmol; n(catalyst 1) = n(catalyst 2) = 0.474 mmol (= 0.5 mol %); m(dioxane) = 85 g.

$[Mo(CO)_6] > [Re_2(CO)_{10}] > [Mn_2(CO)_{10}]$, $[W(CO)_6]$, $[Cr(CO)_6] > [Co_2(CO)_8]$.

Molybdenum hexacarbonyl together with $[Rh(acac)(CO)_2]$ gives the highest yields of 2-ethylheptanol (**4**). Rhenium carbonyl also shows acceptable activities in bimetallic catalysis. The reductions with other carbonyls are rather slow, so that their application does not seem to be useful. The non-toxic molybdenum acetate as well as the cheap cobalt carbonyl are not alternatives because the yields are too poor.

Using group 8 or 9 precursors in combination with the most powerful carbonyl compound, $[Mo(CO)_6]$, the following sequence with decreasing activity is obtained:

$[Rh(acac)(CO)_2] > [Rh(II)acetate] > [Ru(acac)_3] > [Rh(acac)_3] > [Co_2(CO)_8] > [Rh(cod)Cl]_2$, $[RhCl_3 \cdot 3\,H_2O]$.

Compared to $[Rh(acac)_3]$ used by Fuchikami et al.,[6] the activity of $[Rh(acac)(CO)_2]$ is much higher. In general, complexes with oxygen-donor ligands like acetate or acetylacetonate show the best activity in the reduction of carboxylic acids. Surprisingly, $[Rh(cod)Cl]_2$, an excellent catalyst precursor[13] for isomerizations and hydrogenations,[14] is inactive in this type of reaction, probably because of the high dissociation energy of the rhodium-chlorine bond. Furthermore, due to the electronegativity of the chlorine ligands, the electron density at the rhodium atom is substantially reduced making the oxidative addition of hydrogen more difficult. For that reason [$RhCl_3 \times 3\ H_2O$] is inactive, too.

At higher temperatures hydrocarbons are formed in small amounts as the only by-products, while no esters could be detected. To determine the quantity of hydrocarbons in the reaction mixture a sample was analyzed without further distillation (see Run 2/22) by GC with an internal standard. The amount of hydrocarbons is in the range of 5% (GC). Additionally, when the product is distilled a 92% yield (12.57 g) of 2-ethylheptanol (**4**) is obtained.

Using a second, high boiling solvent like propylene carbonate or a long chain hydrocarbon, the product as well as the dioxane can be distilled from the reaction mixture. The catalyst remains in solution and therefore can be recycled, however with decreasing activity.

The results of the reductions with a homogeneously dissolved carbonyl complex and a second heterogeneous catalyst are shown in Table 3.

The yields are not as high as for the completely homogeneously catalyzed reactions. Nevertheless, the heterogeneous compounds have a synergetic effect, accelerating the catalysis. So far, it is not proven where the reaction takes place. One possibility is a reaction at the surface of the heterogeneous catalyst. On the other hand, the reaction could be homogeneously catalyzed because of leaching of the highly dispersed metal.

Another bimetallic catalyst applied in the reduction of 2-ethylheptanoic acid is the rhenium/osmium oxide system, described by Yoshino et al.[4] The experimental results with this bimetallic system are shown in Table 4.

This Re/Os catalyst reduces 2-ethylheptanoic acid with considerable activity. After 2 h at 200 °C and 100 bar hydrogen pressure 55% of 2-ethylheptanol are produced. This yield is even superior to the Rh/Mo-catalyzed reduction at this pressure. However, handling of the highly toxic osmium tetroxide is not convenient for industrial applications. No information is given in the literature whether this reaction is catalyzed homogeneously or heterogeneously.

Reduction of Lactones to Diols

Catalysts that are able to reduce carboxylic acids to alcohols are also active in the reduction of lactones, thus yielding diols. This reaction was carried out using the most active bimetallic catalyst system, the mixture of [$Rh(acac)CO)_2$] and [$Mo(CO)_6$]. The reactants were 2-ethylheptan-5-olide and 2-ethylheptan-4-olide which are produced from butadiene, carbon dioxide, and hydrogen (see Scheme 1). Additionally, the commercially available lactones γ-butyrolactone, γ-valerolactone, δ-valerolactone, and ε-caprolactone were used.

Reduction of 2-Ethylheptan-5-olide to 2-Ethyl-1,5-heptanediol

The reduction of 2-ethylheptan-5-olide (**5**) with hydrogen in the presence of an Rh/Mo bimetallic catalyst leads to 2-ethyl-1,5-heptanediol (**6**). 2-Ethylheptanol (**4**) and 6-methyl-3-octanol (**11**) can be formed in an undesired consecutive reaction (Scheme 3).

The results of the reduction of 2-ethylheptan-5-olide (**5**) are shown in Table 5. The reaction was investigated with respect to temperature, hydrogen pressure, catalyst concentration, and rhodium/molybdenum ratio.

The highest yield is reached at 190 °C and 150 bar hydrogen pressure (Run 5/6). After two hours a 97% yield of **6** is achieved. Longer reaction times lead to product decomposition and alcohol formation (Run 5/7).

Table 3. Reduction of 2-ethylheptanoic acid with homogeneous/heterogeneous bimetallic catalysts.

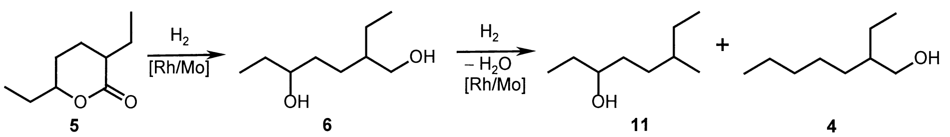
Run	Catalyst 1	Catalyst 2	Temperature [°C]	Pressure H_2 [bar]	Time t [h]	Yield (**4**) [%]
3/1	[$Re_2(CO)_{10}$]	Rh/Al_2O_3	150	130	4	13
3/2	[$Mo(CO)_6$]	Rh/Al_2O_3	200	150	2	21
3/3	[$Mo(CO)_6$]	Rh/Al_2O_3	200	150	2	27
3/4	[$Mo(CO)_6$]	Rh/C	200	150	2	14
3/5	[$Mo(CO)_6$]	Ru/C	200	150	2	69

Conditions: stirrer velocity = 600 rpm; m(**3**) = 2 g; n(**3**) = 12,.6 mmol; n(catalyst 1) = n(catalyst 2) = 0.126 mmol (= 1 mol %); m(dioxane) = 40 g.

Table 4. Reduction of 2-ethylheptanoic acid (3) with rhenium/osmium bimetallic catalysts.

Run	Catalyst 1	Catalyst 2	Temperature [°C]	Pressure H_2 [bar]	Yield (**4**) [%]
4/1	Re(VII) oxide	Os(VIII) oxide	120	150	4
4/2	Re(VII) oxide	Os(VIII) oxide	150	100	14
4/3	Re(VII) oxide	Os(VIII) oxide	200	100	55

Conditions: time t = 2 h; stirrer velocity = 600 rpm; m(**3**) = 2 g; n(**3**) = 0.0126 mol; m(catalyst) = 62.7 mg; m(dioxane) = 40 g.



Scheme 3. Reduction of 2-ethylheptan-5-olide to 2-ethyl-1,5-heptanediol.

Table 5. Reduction of 2-ethylheptan-5-olide (**5**) with rhodium/molybdenum catalysts.

	Conditions		Conversion [wt %]	Yield Products in wt %			Catalyst		
Run	Temperature [°C]	Pressure H_2 [bar]	(**5**)	**6**	**4**	**11**	$[Mo(CO)_6]$ [mol %]	$[Rh(acac)(CO)_2]$ [mol %]	Ratio Mo/Rh
5/1	140	150	0	0	0	0	1.0	1.0	1.0
5/2	150	150	8	8	0	0	1.0	1.0	1.0
5/3	160	150	33	33	0	0	1.0	1.0	1.0
5/4	170	150	48	48	0	0	1.0	1.0	1.0
5/5	180	150	92	92	0	0	1.0	1.0	1.0
5/6	190	150	97	97	0	0	1.0	1.0	1.0
5/7	200	150	100	75	11	14	1.0	1.0	1.0
5/8	180	50	38	38	0	0	1.0	1.0	1.0
5/9	180	100	97	92	2	3	1.0	1.0	1.0
5/10	180	150	92	88	2	2	0.5	0.5	1.0
5/11	180	150	41	40	0	0	0.1	0.1	1.0
5/12	180	150	19	19	0	0	1.0	0.33	3.0
5/13	180	150	13	13	0	0	1.0	0.50	2.0
5/14	180	150	90	62	7	21	0.20	1.0	0.20
5/15	180	150	100	53	14	33	0.33	1.0	0.33
5/16	180	150	79	55	8	16	0.50	1.0	0.50
5/17[a]	180	150	100	96	2	2	1.0	1.0	1.0
5/18[b]	170	100	87	80	0	7	0.5	0.5	1.0

Conditions: stirrer velocity = 600 rpm, t = 2 h, m(solvent = dioxane) = 40 g, m[2-ethylheptan-5-olide (**5**)] = 2 g.

[a] Reaction time = 5h.

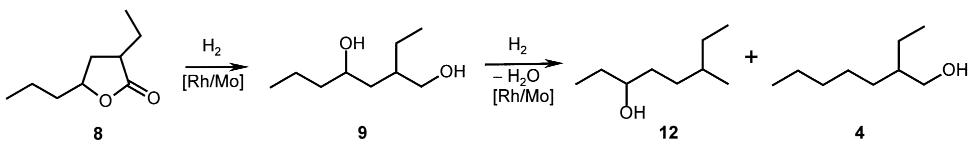
[b] Reaction time = 4 h, m(solvent) = 85 g, m(**5**) = 15 g.

Decreasing the hydrogen pressure from 150 to 100 bar influences the yield of **6** slightly whereas at 50 bar only 38 % product is formed. The ratio of the two transition-metal precursors strongly influences the catalyst activity. Lowering the rhodium amount leads to a great loss of activity, whereas the influence of a lower molybdenum amount is smaller. Presumably, the main catalytic reaction occurs at the rhodium central atom, which is activated by the molybdenum compound. The overall hydrocarbon formation is low. To determine the quantity of hydrocarbons in the reaction mixture a sample was analyzed without further distillation (see Run 5/18) by GC with an internal standard. Only traces of hydrocarbons were detected.

Reduction of 2-Ethylheptan-4-olide to 2-Ethyl-1,4-heptanediol

The reduction of 2-ethylheptan-4-olide (**8**) to 2-ethyl-1,4-heptanediol (**9**) (Scheme 4) is performed analogously to the reduction of the six-membered ring lactone 2-ethylheptan-5-olide (**5**) with the $[Rh(acac)(CO)_2]$/$[Mo(CO)_6]$ catalyst.

The desired main product is 2-ethylheptane-1,4-diol (**9**), whereas the by-products are 2-ethylheptanol (**4**) and 6-methyl-4-octanol (**12**). In addition, a remarkable amount of hydrocarbons is formed. Several reactions with bimetallic rhodium/molybdenum catalyst have been carried out, as summarized in Table 6.



Scheme 4. Reduction of 2-ethylheptan-4-olide to 2-ethyl-1,4-heptanediol.

Table 6. Reduction of 2-ethylheptan-4-olide (**6**) with rhodium/molybdenum catalysts.

Run	Temperature [°C]	Pressure H_2 [bar]	Time [h]	Conversion (**8**) [%]	Yield Hydrocarbons [%]	Yield (**12**) [%]	Yield (**4**) [%]	Yield (**9**) [%]
6/1	180	100	2	14	3	11	0	0
6/2	180	150	2	12	0	8	2	2
6/3	180	150	5	39	9	15	4	11
6/4	180	150	20	72	52	0	5	15

Conditions: m[2-ethylheptan-4-olide (**6**)] = 2 g, m(solvent = dioxane) = 40 g, n(catalyst 1) = n(catalyst 2) = 0.126 mmol (= 1 mol %); m(dioxane) = 40 g.

The yields of 2-ethylheptane-1,4-diol (**9**) are, however, rather low. At longer reaction times the conversion increases causing the formation of by-products like alcohols and hydrocarbons. An increase in product formation is hardly achieved. The reason is the higher thermodynamic stability of five-membered lactone rings compared to six-membered rings[9]. Hence, more thermal energy is necessary to open the lactone ring, which simultaneously causes decomposition of the product. For that reason the yield of product **9** does not increase either at higher temperatures or at longer reaction times.

Comparison of the Reduction of Commercially Available Lactones

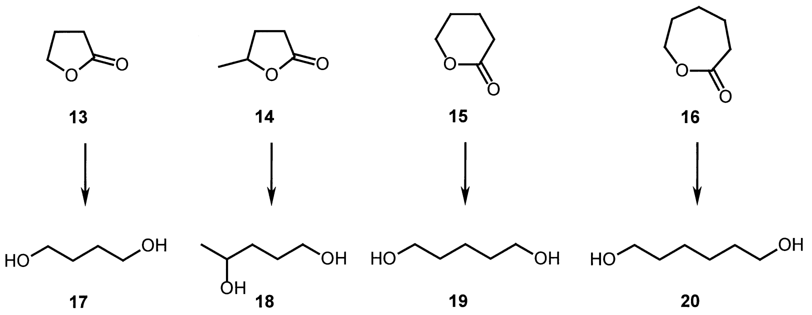
The rhodium/molybdenum catalyst was applied to the reduction of γ-butyrolactone (**13**), γ-valerolactone (**14**), δ-valerolactone (**15**), and ε-caprolactone (**16**) (Scheme 5). The products are the corresponding diols 1,4-butanediol (**17**), 1,4-pentanediol (**18**), 1,5-pentanediol (**19**), and 1,6-hexanediol (**20**).

The reduction is carried out at 150 °C and 100 bar hydrogen pressure. Conversions and yields are summarized in Table 7.

The reduction of these lactones is easier compared to 2-ethylheptan-5-olide (**5**) and 2-ethylheptan-4-olide (**8**) because they are not branched in the α-position to the carboxylic group and therefore sterically less hindered. Additionally, the reactivity of the reactants depends on the ring size of the lactone: the two γ-lactones are more difficult to reduce than the δ- or ε-lactone, confirming the observation made previously.

Conclusion

On searching for new bimetallic homogeneous reduction catalysts, an equimolar mixture of $[Rh(acac)(CO)_2]$ and $[Mo(CO)_6]$ showed the highest activity. This catalyst is very active in the reduction of carboxylic acids to



Scheme 5. Reduction of commercially available lactones.

Table 7. Reduction of commercially available lactones with rhodium/molybdenum catalysts.

Run	Lactone	Conversion Lactone [%]	Products [%] Hydrocarbons	Alcohol	Diol	Selectivity Diol [%]
7/1	γ-Butyrolactone (**13**)	67	0	10	57	85
7/2	γ-Valerolactone (**14**)	54	4	7	43	80
7/3	δ-Valerolactone (**15**)	100	6	19	75	75
7/4	ε-Caprolactone (**16**)	86	0	7	79	92

Conditions: m(lactone) = 5 g, m(dioxane) = 50 g, n(Rh) = n(Mo) = 0.25 mol %, temperature = 150 °C, p(H_2) = 100 bar, t = 3 h.

monoalcohols and also in the reduction of lactones to diols. The advantages compared to heterogeneous copper chromite reductions are the higher yields and the milder reaction conditions. Additionally, the preparation of the catalyst is very simple: the active species is formed *in situ* by dissolving the two commercially available precursors in polar solvents, e.g., dioxane. Non-branched lactones could be reduced at low catalyst concentrations (0.25 mol %) as well as low hydrogen pressures (100 bar) with high activity. TOF's in the range of 100 – 200 h^{-1} are achieved.

Experimental Section

General

All chemicals which were commercially available were used without further purification. 1,4-Dioxane with a water content < 0.05 % was used. The products were identified and characterized by MS, GC/MS, ^{1}H NMR and ^{13}C NMR.

General Procedure

In a typical experiment, 32.6 mg (1.26×10^{-4} mol) [Rh(acac)-$(CO)_2$], 33.4 mg [$Mo(CO)_6$] (1.26×10^{-4} mmol), and 2.00 g (1.26×10^{-3} mol) of 2-ethylheptanoic acid (**3**) were dissolved in 40 g 1,4-dioxane in a Schlenk tube and transferred into an evacuated 300-mL stainless steel autoclave. The vessel was pressurized with 120 bar hydrogen and heated up to 200 °C within 20 min leading to a hydrogen pressure of 150 bar at reaction temperature. The reaction time of 2 h was taken after accelerating the stirrer to 700 rpm. After the reaction mixture was cooled to room temperature the solvent was evaporated. The product was separated from the catalyst by vacuum distillation. A sample of the products was taken and analyzed by gas chromatography with undecyl acetate as internal standard and acetonitrile as solvent.

[OsO_4]/[Re_2O_7] Catalyst

The catalyst was prepared according to[4] by mixing rhenium heptoxide [Re_2O_7] (0.5 g, 1×10^{-3} mol), osmium tetroxide [OsO_4] (1.0 g, 4×10^{-3} mol) and succinic acid (0.87 g, 7.4×10^{-3} mol) in ethyl acetate (26 g). The reduction was carried out at a temperature of 140 °C and at 100 atm of hydrogen pressure in 1 h. The catalyst was filtered and washed several times with ethyl acetate.

2-Ethylheptan-5-olide (5)

Telomerization of carbon dioxide with 1,3-butadiene gave 2-ethylidene-5-hepten-6-olide[10] that was hydrogenated at 10 bar and 60 °C in THF with a commercial Pd/C catalyst. Separation by extraction and distillation gave a mixture of the isomeric 2-ethylheptan-5-olides in yields up to 95%.

2-Ethylheptan-4-olide (8)

Telomerization of carbon dioxide with 1,3-butadiene at longer reaction times gave 2-ethyldidene-4-hepten-5-olide[9] that was hydrogenated at 10 bar and 60 °C in THF with a commercial Pd/C catalyst. Separation by extraction and distillation gave 2-ethylheptan-4-olides in yields up to 95%.

2-Ethylheptanoic Acid (3)

Telomerization of carbon dioxide with 1,3-butadiene gave 2-ethyldidene-5-hepten-6-olide that was hydrogenated at 10 bar and 110 °C with a water-soluble rhodium-tppts (tppts = triphenylphosphinetrisulfonate sodium salt) catalyst giving a mixture of the corresponding unsaturated C_9 acids[7]. These acids were hydrogenated at 10 bar and 60 °C in methanol with a commercial Pd/C catalyst giving 2-ethylheptanoic acid in quantitative yield.

Characterization

2-Ethylheptan-5-olide: diastereomer in square brackets: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.13$ [4.12] [-CH_2-$\underline{CH}$(C_2H_5)-O-CO-, m, 1H], 2.30 [2.27] [-$\underline{CH}$(C_2H_5)-CO-O-, m, 1H], 2.02 + 1.50 [1.98 + 1.58] (-$\underline{CH_2}$-CH-O-CO-, m, 2H), 1.94 + 1.48 [1.95 + 1.58] [-$\underline{CH_2}$-CH(C_2H_5)-CO-O-, m, 2H], 1.88 + 1.62 [1.90 + 1.62] [-CH($\underline{CH_2}$-CH_3)-CO-O-, m, 2H], 1.66 + 1.62 [1.65 + 1.60] [-CH($\underline{CH_2}$-CH_3)-O-CO-, m, 2H], 0.92 [0.93] [-CH(CH_2-$\underline{CH_3}$)-CO-O-, t, ^3J(H,H) = 7.5 Hz, 3H], 0.92 [0.88] [-CH(CH_2-$\underline{CH_3}$)-O-CO-, t, ^3J(H,H) = 7.5 Hz, 3H]; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 175.85$ [174.04], 79.49 [82.72], 39.63 [42.31], 28.49 [29.35], 26.44 [28.52], 24.06 [25.10], 23.09 [25.10], 11.76 [11.24], 9.77 [9.41]; MS: *m/e* = 156 [M^+] (1), 128 (100), 127 (43), 110 (16), 99 (16), 98 (12), 83 (18), 81 (56), 73 (32), 70 (95), 69 (22), 57 (35), 56 (84), 55 (87), 43 (29), 42 (28), 41 (57), 39 (16), 32 (15).

2-Ethylheptan-4-olide: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 4.23 [-$\underline{CH}$(C_3H_7)-O-CO-, m, 1H], 2.41 [-O-CO-$\underline{CH}$(C_2H_5)-CH_2, m, 1H], 2.32 + 1.41 [-CO-O-CH($\underline{CH_2}$-CH_2-CH_3)-, m, 2H], 1.77 + 1.45 [-O-CO-CH($\underline{CH_2}$-CH_3)-, m, 2H], 1.57 + 1.48 [-O-CO-CH(C_2H_5)-$\underline{CH_2}$-, m, 2H], 1.32 [-CO-O-CH($CH_2\underline{CH_2}$-CH_3)-, m, 2H], 0.84 [t, ^{3}J(H,H) = 7.5 Hz, 3H], 0.82 [t, ^3J(H,H) = 7.4 Hz, 3H]; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 178.6$, 78.3, 42.0, 37.3, 34.3, 22.9, 18.3, 13.5, 11.2; MS: *m/e* = 156 [M^+] (4), 128 (45), 113 (100), 110 (10), 85 (22), 83 (13), 70 (23), 69 (17), 67 (17), 57 (22), 56 (38), 55 (39), 43 (28), 42 (14), 41 (45), 39 (11).

2-Ethylheptanoic acid [3274-29-1]: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.77$ (s, 1H), 2.29 (m, 1H), 1.58 (m, 2H), 1.50 (m, 2H), 1.41 (m, 2H), 1.24 – 1.30 (m, 4H), 0.89 [t, ^3J(H,H) = 7.4 Hz, 3H], 0.83 [t, ^3J(H,H) = 7.1 Hz, 3H]; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 183.4$, 47.2, 31.7, 31.7, 27.0, 25.2, 22.5, 13.9, 11.7. MS: *m/e* = 158 [M^+] (3), 130 (11), 101 (26), 88 (100), 87 (13), 73 (54), 55 (11), 43 (14), 41 (15).

2-Ethylheptanol [817-60-7]: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.47$ [d, ^3J(H,H) = 5.1 Hz, 1H], 1.52 (s, 1H), 1.22 – 1.37 (m, 12H), 0.83 [t, ^3J(H,H) = 7.2 Hz, 3H], 0.82 [t, ^3J(H,H) = 7.1 Hz, 3H]; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 65.2$, 42.0, 32.2, 30.4, 26.5, 23.0, 22.6, 14.1, 11.1; MS: m/e = 144 [M^+] (1), 126 (15), 98 (13), 97 (36), 84 (26), 83 (26), 71 (81), 70 (49), 69 (18), 57 (100), 56 (30), 55 (48), 43 (75), 42 (11), 41 (43).

2-Ethyl-1,5-heptanediol: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.57 (m, 1H), 3.55 (m, 1H), 3.35 (s, 2H), 1.39 (m, 6H), 1.25 (m, 4H), 0.93 [t, ^3J(H,H) = 7.5 Hz, 3H], 0.89 [t, ^3J(H,H) = 7.5 Hz, 3H]; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) diastereomer in square brackets: δ = 73.30 [73.81], 64.88 [64.48], 41.73 [42.32], 33.18 [34.00], 30.28 [30.39], 26.04 [26.62], 23.52 [23.96], 11.44 [11.49], 10.18 [10.12]; MS: *m/e* = 160 [M$^+$] (1), 113 (48), 112 (40), 95 (99), 89 (37), 85 (15), 84 (23), 83 (20), 72 (26), 71 (18), 70 (31), 69 (100), 68 (10), 67 (12), 59 (71), 57 (76), 55 (64), 45 (11), 43 (61), 42 (18), 41 (65), 39 (12).

2-Ethyl-1,4-heptanediol [15966-04-8]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.85 (s, 2H), 3.62 (m, 2H), 3.34 [t, ^3J(H,H) = 8.1 Hz, 1H], 1.23 – 1.56 (m, 9H), 0.92 [t, ^3J(H,H) = 6.8 Hz, 3H], 0.90 [t, ^3J(H,H) = 7.5 Hz, 3H]; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 70.9, 66.1, 41.1, 40.9, 40.4, 25.2, 18.8, 13.9, 11.1; MS: m/e = 160 [M$^+$] (1), 117 (38), 113 (10), 112 (34), 99 (92), 83 (14), 81 (41), 73 (21), 72 (40), 71 (21), 69 (20), 57 (47), 56 (20), 55 (100), 43 (84), 42 (33), 41 (40), 39 (10).

Acknowledgements

We would like to thank Dr. B. Costisella for NMR analysis. We are very grateful to Degussa AG for the supply of catalysts and catalyst precursors.

References

[1] K. Noweck, H. Ridder, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 6th Edition, **2001**, Electronic Release, Fatty Alcohols.

[2] M. Biachi, G. Menchi, F. Francalanci, F. Piacenti, U. Matteoli, P. Frediani, C. Botteghi, *J. Organomet. Chem.* **1980**, *188*, 109 – 119.

[3] a) H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1997**, 667 – 668; b) H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1998**, 1367 – 1368.

[4] K. Yoshino, Y. Kajiwari, N. Takaishi, Y. Inamoto, J. Tsuji, *J. Am. Oil Chem. Soc.* **1990**, *67*, 21 – 24.

[5] M. Kitson, P. S. Williams (BP Chemicals Limited), *Eur. Patent* 0198682, **1986**; *Chem. Abstr.* **1989**, *111*, 6918.

[6] D.-H. He, N. Wakasa, T. Fuchikami, *Tetrahedron Lett.* **1995**, *36*, 1059 – 1062.

[7] A. Behr, V. A. Brehme, *J. Mol. Catal.* **2002**, in press.

[8] A. R. Elsagir, *PhD thesis*, Friedrich-Schiller-Universität Jena (Germany), **1997**.

[9] a) A. Behr, K.-D. Juszak, *J. Organomet. Chem.* **1983**, 255, 263 – 268; b) P. Braunstein, D. Matt, D. Nobel, *J. Am. Chem. Soc.* **1988**, 110, 3207 – 3212.

[10] A. Musco, R. Santi, G. P. Chiusoli (Montedison S. p. A.), *US Patent* 4,167,513, **1979**; *Chem. Abstr.* **1979**, *90*, 186403.

[11] a) B. Hileman, *Chem. Eng. News* August 7, **2000**, 52 – 54; b) B. Hileman, *Chem. Eng. News* Januar 3, **2000**, 8 – 9.

[12] K. Suda, K. Fujino, M. Yagi, T. Mitsuta, Y. Iwata (Kawakami Paint Mfg, Japan), *Patent JP* 05285451 A2, **1993**; *Chem. Abstr.* **1994**, *120*, 220522.

[13] W. A. Herrmann, *Double Bond Isomerization of Olefins*, in *Applied Homogeneous Catalysis with Organometallic Compounds*, (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2000**, 980 – 991.

[14] H. Brunner, *Hydrogenation.* in *Applied Homogeneous Catalysis with Organometallic Compounds*, (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2000**, 201 – 219.

[15] A. Behr, K.-D. Juszak, W. Keim, *Synthesis* **1983**, 574.